Ambient Air Concentrations of Benzene in Canada (1989-1998)

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Ambient Air Measurements of Benzene in Canada (1989-1998)

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Executive Summary

The Analysis and Air Quality Division of the Environmental Protection Service, Environment Canada (EC) has operated a field measurement program for benzene and other volatile organic compounds (VOCs) in ambient air since 1989. With the cooperation of provincial and municipal environmental agencies, samples have been collected at over 50 urban and rural monitoring sites across the country. The collected data from the monitoring program are used to assess population exposure to benzene and other air toxics as well as to support photochemical oxidant assessment and control activities. Previous reports and publications on the results of the program have been prepared and distributed. This paper provides an update on these earlier works and was prepared additionally as a supporting document for the proposed Canada Wide Standard (CWS) for benzene. Results from an Ontario Ministry of Environment (OME) benzene monitoring program (17 additional unique sites) are also included in the data analysis. Sites are compared based on location (rural, suburban and urban) and in terms of source influences (transportation and industrial). Seasonal and day of week variations in benzene concentrations are examined and trends in benzene levels over the period are analyzed for sites with complete data.

Samples are normally collected over 24-h sampling periods once every six days. At many sites, more intensive VOC sampling campaigns have been carried out (to support the ground level ozone science program) with samples collected over three, four or twelve hour sampling periods. Ambient air samples are collected in stainless steel canisters and analyzed using a cryogenic pre-concentration technique with a high-resolution gas chromatograph and quadropole mass-selective detector (GC-MSD).

An extensive database of ambient air benzene observations is available for Canada for the 1989 to 1998 time period. Mean benzene concentrations (using data for all years) ranged from 10.3 $\mu g/m^3$ at an urban site influenced by emissions from a coke oven/iron and steel mill facility (Sault Ste. Marie-Bonney St.) to 0.3 $\mu g/m^3$ at a rural remote site (Kejimkujik National Park in Nova Scotia). For typical (i.e. not adjacent to roadways) urban site locations with no industrial source influences, mean benzene concentrations over the period were in the range of 1.8 to 3.6 $\mu g/m^3$. Mean and median benzene concentrations are highest at urban-street sites and at sites influenced by industrial sources and lowest at rural and suburban sites.

For the most recent years of measurements (1995 to 1997), mean concentrations at the urban/suburban sites ranged from 1.0 to 3.5 $\mu g/m^3$ with most sites (31 out of 40) recording mean concentrations of less than 2.5 $\mu g/m^3$. Ninetieth percentile concentrations at these sites ranged from 1.5 to 6.6 $\mu g/m^3$ with most sites (31 out of 40) recording 90th percentile concentrations of less than 4.5 $\mu g/m^3$. For the rural sites mean concentrations ranged between 0.3 and 0.8 $\mu g/m^3$ with 90th percentile concentrations ranging between 0.6 and 1.7 $\mu g/m^3$. For sites near roadways or near industrial sources, mean benzene concentrations ranged from 4.1 to 13.1 $\mu g/m^3$ and 90th percentile concentrations varied from 8.0 to 36.0 $\mu g/m^3$.

Most sites recorded decreases in benzene concentrations between 1990 and 1997. Using the composite results for urban sites with complete data there was a 25% reduction in annual mean benzene concentrations between 1990 and 1995 followed by a small increase between 1996 and 1997. Results for individual sites are quite variable with percentage reductions between 1990 and 1996 ranging from 0 to 50 %. A number of sites with the highest mean concentrations showed little or no improvement over the period.

A complete emission inventory trend analysis has not yet been completed, but the decline in ambient benzene levels at most urban sites is a result of improved VOC emission control technology on new motor vehicles plus the effect of reduced gasoline benzene levels. The relationship between emissions and ambient levels of benzene will be explored in a later report. The lack of improvement in benzene levels at some sites with high concentrations will also be investigated.

Sommaire

Depuis 1989, la Division de l'analyse et de la qualité de l'air du Service de protection de l'environnement, d'Environnement Canada (EC), gère un programme de mesures sur le terrain des concentrations de benzène et d'autres composés organiques volatils (COV) présents dans l'air ambiant. Grâce à la collaboration des ministères provinciaux et des autorités municipales responsables de l'environnement, des échantillons ont été prélevés à plus de 50 sites de surveillance en milieux urbain et rural dans tout le pays. Les données recueillies dans le cadre de ce programme de surveillance servent à évaluer le degré d'exposition de la population au benzène et à d'autres substances atmosphériques toxiques, de même qu'à appuyer l'évaluation des polluants oxydants photochimiques et les activités de vérification. Des rapports et publications antérieurs sur les résultats du programme ont été compilés et distribués. Le présent document, qui est un ajout, fournit une mise à jour des premiers travaux et sert de document d'appui aux normes pancanadiennes sur le benzène (CWS). Les résultats d'un programme de surveillance des concentrations de benzène (à 17 sites uniques additionnels) du ministère de l'Environnement de l'Ontario (MEO) sont également visés par l'analyse de données. Les comparaisons établies entre les sites sont basées sur leur emplacement (en milieux rural, suburbain et urbain) et sur l'incidence des sources (véhicules, industries). Les variations dans les concentrations de benzène sont examinées d'une saison et d'une journée à l'autre et les tendances qui se dégagent au cours de la période visée sont analysées pour les sites qui présentent des données complètes.

Les échantillons couvrent généralement une période de 24 heures et sont prélevés une fois tous les six jours. Cependant, de nombreux sites ont fait l'objet de campagnes plus intensives d'échantillonnage des COV (en appui au programme scientifique sur l'ozone troposphérique) avec des périodes couvrant trois, quatre ou douze heures. Les échantillons d'air ambiant sont recueillis dans des contenants en acier inoxydable et analysés à l'aide d'une cryotechnique de préconcentration et d'un chromatographe en phase gazeuse à haute résolution et discriminateur de masse quadripôle (appareil de CG-SM).

Les observations de l'air ambiant effectuées au Canada de 1989 à 1998 sont stockées dans une vaste banque de données. Les concentrations moyennes de benzène (basées sur l'ensemble des données) vont de 10,3 $\mu g/m^3$ dans un site urbain exposé à des émissions provenant d'un four à coke/usine sidérurgique (Sault Ste. Marie-Bonney St.) à 0,3 $\mu g/m^3$ dans un site éloigné en milieu rural (parc national de Kejimkujik en Nouvelle-Écosse). Dans un site type en milieu urbain (c.-à-d. loin d'une route) qui n'est pas exposé à des sources industrielles, les concentrations moyennes de benzène pendant la période visée varient de 1,8 à 3,6 $\mu g/m^3$. Les concentrations moyennes et médianes de benzène sont plus élevées aux sites situés à proximité de voies urbaines et aux sites exposés à des sources industrielles, et plus faibles aux sites en milieux rural et suburbain.

Les mesures effectuées dans les dernières années (1995 à 1997) montrent que les concentrations moyennes aux sites en milieux urbain et suburbain se situent entre 1,0 et

3,5 µg/m^3 avec une majorité de sites (31 sur 40) enregistrant des concentrations moyennes inférieures à 2,5 µg/m^3. À ces sites, le quatre-vingt-dixième percentile varie de 1,5 à 6,6 µg/m^3 avec une majorité de sites (31 sur 40) enregistrant des concentrations au quatre-vingt-dixième percentile inférieures à 4,5 µg/m3. Aux sites en milieu rural, les concentrations moyennes se situent entre 0,3 et 0,8 µg/m^3 avec le 90 ^{ième} percentile variant de 0,6 à 1,7 µg/m^3. Aux sites proches de voies urbaines ou de sources industrielles, les concentrations moyennes de benzène se situent entre 4,1 et 13,1 µg/m^3 avec le 90 ^{ième} percentile variant de 8,0 à 36,0 µg/m^3.

La plupart des sites ont enregistré une baisse des concentrations de benzène entre 1990 et 1997. À l'aide de ces résultats composés pour les sites en milieu urbain et des données complètes, on constate une réduction de 25 % des concentrations moyennes annuelles de benzène entre 1990 et 1995 suivie d'une faible augmentation de 1996 à 1997. Les résultats obtenus à chacun des sites varient grandement, avec des réductions de pourcentages allant de 0 à 50 % de 1990 à 1996. Pour un certain nombre de sites où les concentrations moyennes sont les plus élevées, on a observé une amélioration nulle ou négligeable au cours de cette période. On n'a pas encore terminé l'analyse des tendances basée sur l'inventaire complet des émissions, mais on peut néanmoins affirmer que la baisse des concentrations de benzène dans l'air ambiant à la plupart des sites en milieu urbain est attribuable, d'une part, à l'amélioration des technologies des nouveaux systèmes antipollution des voitures qui réduisent davantage les émissions des COV et, d'autre part, à l'abaissement de la teneur en benzène dans l'essence. Un autre rapport traitera ultérieurement du lien entre les émissions et les concentrations de benzène dans l'air ambiant. Il examinera également l'absence de mesures visant à diminuer les concentrations élevées de benzène à certains sites.

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Introduction

The Analysis and Air Quality Division of the Environmental Protection Service, Environment Canada (EC) has operated a field measurement program for benzene and other volatile organic compounds (VOCs) in ambient air since 1989. With the cooperation of provincial and municipal environmental agencies, samples have been collected at over 50 urban and rural monitoring sites across the country. The collected data from the monitoring program are used to assess population exposure to benzene and other air toxics as well as to support photochemical oxidant assessment and control activities. Previous reports and publications have been prepared and distributed[1,2]. This paper provides an update on these earlier works and was prepared additionally as a supporting document for the proposed Canada Wide Standard (CWS) for benzene. Results from an Ontario Ministry of Environment (OME) benzene monitoring program are also included in the data sets. Sites are compared based on location (rural, suburban and urban) and in terms of source influences (transportation and industrial). Seasonal and day of week variations in benzene concentrations are examined and trends in benzene levels over the period are analyzed for sites with complete data.

Sampling Schedule And Sites

A listing of the benzene sampling sites is provided in Table 1. The table includes the start date for sampling, the number of samples collected, the location of the site (urban, rural or suburban and an indication of potential industrial source influences. The location of the sites is shown in Figure 1. Sampling began at most sites between 1989 and 1992 and benzene data are currently available through mid 1998 for the Environment Canada sites and through 1996 fcr the OME sites. Monitoring data are available from seventy-two individual sites. Most of the sites are situated in urban or suburban areas but fourteen sites are in rural locations. The Ottawa, Montreal-Maisonneuve and Vancouver-Robson Square sites are located close to street level in the urban core and are categorized as urban-street sites. The Toronto-Evans Ave. site is located within 50 m of a major expressway and is also categorized as an urban-street site. Seventeen of the sites are potentially impacted by industrial emissions of benzene. OME data are available from twenty-four sites, seven of which are also represented by EC measurements. Trend analysis was performed on subsets of urban and suburban monitoring sites that had complete data for specified measurement periods (1990 to 1997 or 1992 to 1997). These sites are shown in the table. For rural sites, trend analysis was performed on sites with observations for the 1994 to 1997 period. The final column of the table shows the short-form identification of the site in subsequent figures.

Samples are normally collected over 24-h sampling periods once every six days. At many sites, more intensive VOC sampling campaigns have been carried out (to support the ground level ozone science program) with samples collected over three, four or twelve hour sampling periods.

Table 1: List of Benzene Monitoring Sites and Summary of Available Data (as of Dec. 1998).

NAPS No.	City[1]	Address	Site Classification	Industrial Source Impact[2]	Start Date	End Date	24h Sampling	3,4 or 12h Sampling	Trend Site (Years)	Figure 1 Site ID
30117	Halifax	Bedford Row P.O.	Urban		09-Jun-89	08-Oct-90	X			
30118	Halifax	1657 Barrington	Urban		07-Dec-90	10-Jun-98	X		92-97	Halifax
30501	Kejimkujik National Park		Rural		06-Jun-94	07-Sep-97		X	94-97	Kejimkujik
40501	Pt. Lepreau	Main Gate	Rural		05-Jul-92	16-Feb-98	X		94-97	Lepreau
40203	Saint John	Forest Hills	Suburban	R	24-May-92	16-Feb-98	X	X	92-97	Saint John
50103	Montreal	Pte. aux Trembles	Suburban	R,C	16-Jan-89	03-Aug-98	X	X	90-97, 92-97	Mon-PT
50104	Montreal	1125 Ontario St.	Urban		10-May-89	22-Jul-98	X		90-97, 92-97	Mon-ONT
50115	Montreal	1001 Maisonneuve O.	Urban-Street		09-Jul-92	03-Aug-98	X	X	92-97	Mon-MAIS
50121	Montreal	Parc Oceanie, Brossard	Suburban		30-Jun-93	22-Jul-98	X			Mon-BROS
54101	Mount Sutton		Rural		06-Jun-94	26-Sep-98		X	94-97	Sutton
54301	Ste. Francoise		Rural		26-Feb-93	05-May-98		X	94-97	Ste. Francoise
54401	St. Anicet		Rural		15-Jun-94	30-Dec-97		X	94-97	St. Anicet
54501	L'Assomption		Rural		27-May-96	30-Dec-97		X		L'Assomption
60101	Ottawa	88 Slater St.	Urban-Street		28-May-89	22-Jul-98	X		90-97, 92-97	Ott-SLA
60104	Ottawa	Rideau/Wurtemburg	Urban		22-Sep-93	28-Jul-98	X			Ott-WURT
60204	Windsor	467 University Ave.	Urban		04-Jan-89	08-Apr-94	X	X		Win-UNI
60204	Windsor[1]	467 University Ave.			04-Feb-90	17-Dec-96	X			
60211	Windsor	College/Prince	Urban		29-May-90	29-Jan-98	X	X	90-97, 92-97	Win-CP
60212	Windsor[1]	Wright/Water	Urban	I&S	28-Jun-90	17-Dec-96	X			Win-WW
-	Windsor[1]	St. Gabriel's School	Suburban		01-Jan-92	20-Mar-93	X			
-	Windsor[1]	Geo. P. Vanier School	Suburban		01-Jan-92	20-Mar-93	X			
60403	Toronto	Evans/Arnold	Urban-Street		18-Jun-95	04-Feb-98	X	X		Tor-EVAN
60403	Toronto[1]	Evans/Arnold			30-Jul-93	19-Feb-94	X			
60424	Toronto	Bay/Grosvenor	Urban		06-May-92	18-Sep-95	X	X		Tor-BAY
60422	Toronto	35 Edgar Ave.	Urban		04-Jan-89	25-Apr-93	X			
60418	Toronto	Junction Triangle	Urban		04-Jan-89	04-Feb-98	X			Tor-JT
60418	Toronto[1]	Junction Triangle			16-Feb-90	02-Dec-92	X		90-97, 92-97	
60413	Toronto	Elmcrest Road	Suburban		01-May-93	04-Feb-98	X	X		Tor-ELM
60426	Mississauga	Clarkson Refinery	Suburban	R	02-Jul-96	04-Feb-98	X			
-	Mississauga	Meadow Park	Suburban		23-Jun-91	19-Feb-94	X			
60512	Hamilton	Elgin/Kelly	Urban	I&S	28-Jan-89	04-Jul-98	X		90-97, 92-97	Ham-ELG
60512	Hamilton[1]	Elgin/Kelly			16-Jan-90	17-Dec-96	X			
60511	Hamilton[1]	Beach Boulevard	Suburban	I&S	05-Jul-91	05-Dec-96	X			Ham-BEA
	Hamilton[1]	Gertrude/Depew	Suburban	I&S	13-Mar-92	17-Dec-96	X			Ham-GER
60513	Hamilton[1]	Vicker's/East 18th	Suburban	I&S	23-Jun-91	17-Dec-96	X			Ham-VICK

Table 1 cont'd: List of Benzene Monitoring Sites and Summary of Available Data (as of Dec. 1998).

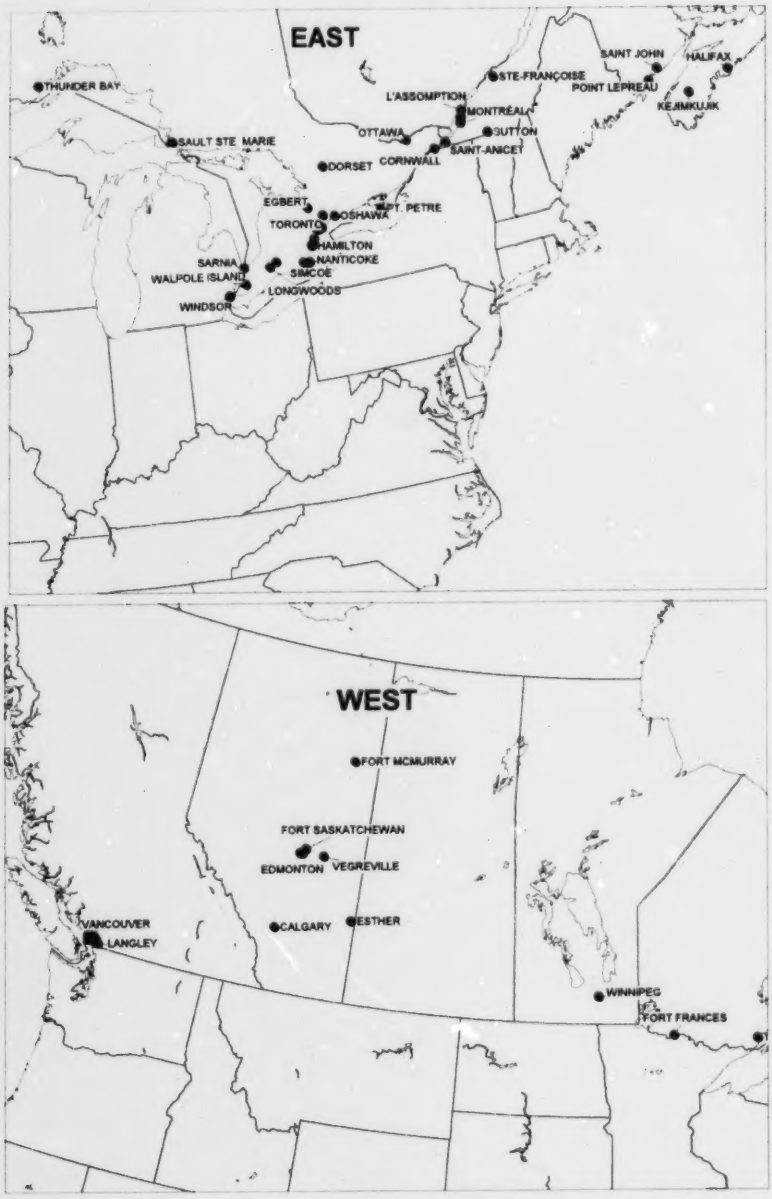
NAPS No.	City[1]	Address	Site Classification	Industrial Source Impact[2]	Start Date	End Date	24h Sampling	3,4 or 12h Sampling	Trend Site (Years)	Figure 1 Site ID
	Hamilton[1]	Pier 25	Suburban	I&S	25-Jan-92	17-Dec-96	X			Ham-P25
	S.S. Marie[1]	Bonney St.	Urban	I&S	14-Jan-94	17-Dec-96	X			S.S.M-BO
60707	S.S. Marie[1]	Wm. Merrifield School	Suburban		02-Oct-90	17-Dec-96	X			S.S.M-W
60807	Thunder Bay[1]	James St. South	Urban		27-Oct-90	17-Dec-96	X			Thunder Bay
60901	London[1]	King/Rectory	Suburban		26-Jan-94	26-Jun-95	X			London
	London[1]	Commissioner's Road	Suburban		12-Apr-91	09-Dec-93	X			
60903	London[1]	Highbury Avenue	Suburban		08-Jul-95	17-Dec-96	X			
	Elmira[1]	Park/Duke	Suburban	C	25-Apr-93	27-May-96	X			Elmira
61004	Sarnia	Centennial Park	Suburban	R,C	10-Jan-89	10-Feb-98	X		90-97, 92-97	Sarnia
61201	Cornwall[1]	Memorial Park	Urban		06-Apr-92	05-Dec-96	X			Cornwall
61602	Oakville	Bronte Rd./Woburn Cres.	Suburban		27-Apr-95	02-Jun-96	X			Oakville
61602	Oakville[1]	Bronte Road/Woburn Cr			23-Jun-91	19-Feb-94	X			
61701	Oshawa[1]	Ritson Road/Olive Ave	Suburban		23-Jun-91	19-Feb-94	X			
61901	Walpole Island		Rural		03-Feb-89	22-Mar-95	X			
62601	Simcoe	Experimental Farm	Rural		06-Feb-93	10-Jul-98	X	X	94-97	Simcoe
63601	Longwoods	Longwoods Cons. Auth.	Rural		12-May-91	10-Feb-98	X		94-97	Longwoods
63201	Stouffville	Hwy 47 & Hwy 48	Suburban		10-Jan-89	04-Feb-98	X		90-97, 92-97	Tor-STOU
63301	Dorset[1]		Rural		19-Mar-91	17-Dec-96	X			Dorset
63801	Nanticoke	Nanticoke Village	Suburban	I&S	13-Jan-93	08-May-94	X			Nan-VIL
63801	Nanticoke[1]	Nanticoke Village			14-May-94	17-Dec-96	X			
63802	Nanticoke	South Walpole	Suburban		25-Jan-93	09-May-94	X			Nan-WAL
063802	Nanticoke[1]	South Walpole			14-May-94	17-Dec-96	X			
64401	Egbert	CARE	Rural		14-Jun-94	17-Sep-98		X	94-97	Egbert
64501	Fort Frances	Church St.	Urban		08-Apr-94	17-Dec-96	X			Fort Frances
64601	Point Petre		Rural		25-Aug-96	16-Feb-98	X			Point Petre
70119	Winnipeg	65 Ellen St.	Urban		24-Dec-89	04-Feb-98	X		90-97, 92-97	Winnipeg
90121	Edmonton	17 St./105 Ave.	Suburban	R,C	27-Aug-90	22-Jul-98	X		90-97, 92-97	Edm-EIMU
90130	Edmonton	10255-104th St.	Urban		18-May-91	22-Jul-98	X		92-97	Edm-EDMU
90227	Calgary	611-4TH ST. SW	Urban		09-Aug-90	04-Jun-98	X		90-97, 92-97	Calgary
90701	Fort McMurray	MacDonald Drive	Suburban		03-Apr-95	31-May-95	X			Fort McMurray
90601	Fort Saskatchewan	100 Ave. & 98th St.	Suburban		28-Dec-94	02-Feb-95	X			
90901	Vegreville	Royal Park	Rural		01-Aug-96	02-Nov-96	X			Vegreville
91001	Esther		Rural		25-Sep-96	30-Nov-96	X			Esther
100112	Vancouver	Robson Square	Urban-Street		28-Jan-89	04-Feb-98	X	X		Van-T1

Table 1 cont'd: List of Benzene Monitoring Sites and Summary of Available Data (as of Dec. 1998).

NAPS No.	City[1]	Address	Site Classification	Industrial Source Impact[2]	Start Date	End Date	24h Sampling	3,4 or 12h Sampling	Trend Site (Years)	Figure 1 Site ID
100118	Vancouver	2550 W 10TH Ave.	Urban		26-Jul-93	06-Aug-93	X			
100110	Vancouver	Kensington Park	Urban	R	04-Jan-89	17-Jan-98	X	X		Van-T4
100121	Vancouver	75 Riverside Dr.	Urban		22-Sep-93	09-Mar-94		X		Van-T6
100111	Vancouver	Rocky Point Park	Urban	R	04-Jan-89	04-Feb-98	X	X	90-97, 92-97	Van-T9
10^127	Vancouver	Surrey East	Suburban		10-Jan-89	11-Jan-98	X			Van-T15
101201	Vancouver	Pitt Meadows Airport	Suburban		15-Sep-92	03-Sep-95		X		Van-T16
100128	Vancouver	Richmond South	Suburban		22-Jan-89	30-Dec-97	X	X		Van-T17
100133	Vancouver	7815 Shellmount St.	Suburban	T	18-Mar-90	17-Jan-98	X		92-97	Van-T22
100132	Vancouver	Mahon Park	Urban		23-May-90	23-Jan-98	X			Van-T26
101301	Vancouver	52nd. Ave. Langley	Suburban		12-Jul-93	05-Jan-98	X	X		Van-T27

[1] OME Monitoring Data [2] R-Refinery, C-Chemical Manufacturing, I&S- Iron & Steel, T-Pipeline Transfer

Figure 1: Monitoring Site Locations: Eastern and Western Canada



Methodology

Environment Canada Sampling & Analysis Methods

Ambient air samples are collected in 6-L stainless steel Summa™ polished canisters (Scientific Instrumental Specialists, Inc. or BRC Rasmussen). The canisters are cleaned and evacuated before shipment to the sampling sites. Sixteen canisters are cleaned simultaneously by evacuation to a vacuum of < 700 Pa with a two-stage vacuum pump and a liquid nitrogen trap. While under vacuum, the canisters are heated to 80 °C. The canisters are then pressurized to 200 kPa with humidified zero air from a pure air generator (AADCO Corp.). This cycle is repeated six to ten times. Two to three canisters of each batch of sixteen are analyzed for VOC to verify that the canisters are clean before the final evacuation.

In the field, ambient air samples are collected in canisters using whole air samplers. Many of the samplers were built in house and are based on the US Environmental Protection Agency (EPA) "R-Type" design[3]. In recent years, samplers have been purchased from Xontech, Inc. (Model 910). Before use, all samplers are cleaned and certified according to the procedures described in EPA method TO-14.[4]

The samplers are programmed to begin drawing ambient air at least 3 min prior to the 24-hour scheduled sample collection period. This is done to purge the sample lines and the pump with ambient air. The pump draws air at a flow-rate of 1 to 2 L/min. The sample flow is split to a mass flow controller that allows a constant flow of 10 to 15 ml/min to the canister with the remaining air exhausted. Canister samples are shipped to the laboratory and typically arrived under 70 to 140-kPa pressure.

The ambient air samples are analyzed using a cryogenic pre-concentration technique with a high-resolution gas chromatograph and quadropole mass-selective detector (GC-MSD) as described in EPA Method TO-14. Two separate automated pre-concentration GC systems are used for analysis. One employs a Nutech 3550A pre-concentrator with auto-sampler (Nutech Corp., Research Triangle Park, N.C.). The other employs an Entech Model 2000 pre-concentrator with auto-sampler (Entech Corp., Calif.). The instruments used for species identification and quantification are a Hewlett Packard 5890 series II GC and a Hewlett Packard 5970 MSD. VOCs are separated on a 50 m, 0.32 mm ID fused silica capillary column with a 1.0-µm film thickness of HP-1 bonded liquid phase.

Approximately 0.5 L of the canister sample is passed through a Nafion dryer to remove water vapour. A mass flow controller is used to measure sample volume and internal standards are added using an internal sample loop in the Nutech system. A cryogenic trap, held at -150 °C, is used to concentrate the air sample. Once the sample is concentrated, the trap is heated to 150°C and the sample is back-flushed onto a cryo-focus located at the head of the silica column. When the GC-MSD is ready, the cryo-focus is heated and the VOCs are injected into the GC. The initial column temperature of -60 °C is held for 3 minutes then raised to 250 °C at 8 °C/min. Operated in selected ion monitoring (SIM) mode, the GC-MSD acquires data for target compounds only and ignores all others. Peak identification is based on GC retention time and MSD confirmation. Benzene and approximately 110 other VOC species are quantified in the samples.

Typical method detection limits for benzene are 0.1 $\mu g/m^3$ for GC-MSD SIM analysis. Method precision as demonstrated by replicate analysis of canister samples is in the range of 5-8 % for concentrations greater than 0.25 ug/m3. The static dilution standards prepared in the laboratory have been compared with a diluted National Institute of Standards and Technology (NIST) aromatic hydrocarbon standard and found to agree within +5%. The laboratory also has participated in the National Centre for Atmospheric Research (NCAR) inter-comparison study for 16 hydrocarbons (NOMHICE)[3] and results for benzene agreed within 3%.

Ontario Ministry of Environment Sampling & Analysis Methods

Routine sampling for ambient air concentrations of VOC evolved out of the Ministry's experience in mobile air monitoring. The first mobile air monitoring vehicles were vans equipped with gas chromatographs for on-site analysis of samples collected on adsorbent tubes. These same adsorbent tubes were adopted for routine network sampling of VOC. Some adjustments were necessary, such as reducing the flow rate to prevent breakthrough during a 24-hour collection, however, for the most part, the mobile technique was directly transferable to fixed site monitoring.

The sampling system uses two or three carbon molecular sieve (CMS) adsorbents in series. Generally, compounds trapped by this method are non-polar, non-reactive organics with boiling points in the -15 to +120 °C range. Ambient air is drawn over the CMS adsorbents at a rate consistent with the breakthrough properties of the sorbents in use. Airflow is regulated by a Tylan Model FC-280 mass flow controller calibrated at the factory for 0-50 ml of air. Airflow passes first over the sorbent specific to heavier molecules before passing over the sorbent specific to lighter molecules. During analysis, the airflow is reversed such that the heavier molecules come off the sorbents first.

A 24-hour sample is collected once every 12 days. A programmable timer is used to turn the sampler on and off and an elapsed time indicator is used to confirm sampler operation. At sites with telemetry systems, the VOC sampler may be attached to the telemetry system to confirm on/off day and time and average hourly flow rate.

Improvements in sorbent technology and analytical methods were incorporated during the monitoring program and these are described below.

1989-1992

Initially, the sampling train consisted of a two-stage CMS trap and a portable sampling pump.The adsorbents in use were Carbotrap "B" (0.2 g; 20/40 mesh; bed height about 20 mm), to collect organic compounds in the C4-C5 range and heavier, and Carbosieve "S" (0.04 g; 60/80 mesh; bed height about 30 mm), to collect smaller airborne molecules such as the C2 hydrocarbons. Cartridges were prepared by Laboratory Services Branch personnel.[4]

During 1989, early in the testing phase, it became apparent that the portable personal samplers were not well suited to 24-hour operation and so the portable pumps were replaced with a metal

bellows pump connected to AC power. The mass flow controller regulated the sampling rate at 25 ml/min to yield a 36-L sample over the 24 hr sampling period.

After sample collection, the adsorbent tube was analyzed by thermal desorption-dual capillary column gas chromatography (GC) with dual flame ionization detectors (FID). Sample tubes were placed in a Metrex Instruments thermal desorption unit and the VOC were thermally desorbed into a helium gas flow. A Nafion dryer was used to remove water from the sample and this resulted in the loss of some compounds, particularly polar compounds. The sample was then cryogenically pre-focused and flash vapourized onto the dual capillary columns for analysis by GC-FID. Identification and quanititation of the VOC was based on a retention index and relative response factor approach.

The calibration of the data system for VOC analysis consisted of an initial calibration and then daily re-calibration. The initial calibration involved the development of a retention index (RI) and relative response factor (RRF) library for the target analytes and a minimum three-point calibration to determine the linear operating range for each analyte. Daily re-calibration involved the analysis of a ten-component n-alkane mixture (C_3-C_{12}) to update the retention index file and to calculate the overall response factor for that day's analyses. Typical detection limits ranged between 0.1 and 1.0 $\mu g/m^3$ based on a 36-L sample. Complete details are available in the Laboratory Services Branch publication DESORB-E3131A.1.[4]

1993-Present

Starting with the first sample collection in 1993, the sampling tube was changed to a commercially available three-stage adsorbent cartridge (Supelco, Mississauga) and the analytical method was changed to gas chromatography with a mass selective detector (GC-MSD). This configuration is in current use.

The three sorbents in the tube are Carbopak B, Carbopak C and Carbosieve S-III. The thermal desorption GC-MSD system consists of a modified Tekmar 4210 auto-sampler, a Tekmar 5010 thermo-desorber, and a Hewlett-Packard 5890 GC with a 5971 low resolution mass spectrometer. Atmospheric moisture is removed by dry purge. Prior to the dry purge, deuterium-labelled surrogates are added to monitor the desorption efficiency, possible breakthrough, and equipment stability problems.

For the first year of operation, detection limits did not change (0.1 to 1.0 $\mu g/m^3$ based on a 7.2 L sample), however, from early 1994 onwards, detection limits improved to 0.02 to 0.2 $\mu g/m^3$ based on a 7.2 L sample. Complete details are available in the Laboratory Services Branch publication MOEE Method E3314.[5]

RESULTS AND DISCUSSION

Ambient Air Benzene Concentrations

There were approximately 20,000 individual benzene observations in the database as of December 1998. Table 2 provides frequency distributions, maximum, mean, standard deviation and median benzene concentrations ($\mu g/m^3$) by site for the all EC and OME data collected between 1989 to 1998 (OME data only available to 1996). For most of the sites, the statistics are based on 24-h data but for some of the rural sites, shorter time period observations are used.

Mean benzene concentrations (using data for all years) ranged from 10.3 $\mu g/m^3$ at the Sault Ste. Marie-Bonney St. site to 0.3 $\mu g/m^3$ at the Kejimkujik site in Nova Scotia. For typical (i.e. not adjacent to roadways) urban site locations with no industrial source influences, mean benzene concentrations over the period were in the range of 1.8 to 3.6 $\mu g/m^3$. The highest 24-h average benzene concentration of 126 $\mu g/m^3$ was measured at the Montreal-Trembles site in 1993. Mean and median benzene concentrations are highest at urban-street sites and at sites influenced by industrial sources and lowest at rural and suburban sites.

As discussed later in the paper, there has been a decrease in benzene recorded at most of the urban monitoring sites between 1989 and 1997 (OME data only available to 1996). In Figure 2, sites are compared in terms of current (1995/97) benzene concentrations using a boxplot presentation. The rural sites are shown separately from urban/suburban sites, as are the seven sites with the highest mean concentrations (greater than 4.0 $\mu g/m^3$). Figure 3 shows the data for the rural and urban sites only (excluding the highest sites) so that differences between sites are more easily seen. For the rural sites mean concentrations ranged between 0.3 and 0.8 $\mu g/m^3$ with 90^{th} percentile concentrations ranging between 0.6 and 1.7 $\mu g/m^3$. The highest concentrations were measured at the rural sites closest to cities such as l'Assomption, Simcoe and Longwoods. Rural concentrations appear higher at sites in Ontario and Quebec than at sites in the Atlantic and Prairie regions, although there are very few observations from rural western sites. Mean concentrations at the urban/suburban sites ranged from 1.0 to 3.5 $\mu g/m^3$ with most sites (31 out of 40) recording mean concentrations of less than 2.5 $\mu g/m^3$. Ninetieth percentile concentrations at these sites ranged from 1.5 to 6.6 $\mu g/m^3$ with most sites (31 out of 40) recording 90^{th} percentile concentrations of less than 4.5 $\mu g/m^3$. For the highest concentration sites, mean benzene concentrations ranged from 4.1 to 13.1 $\mu g/m^3$ and 90^{th} percentile concentrations varied from 8.0 to 36.0 $\mu g/m^3$.

Table 2: Summary Statistics for Benzene (µg/m³): 1989 – 1998

Agency	City	Address	Start Date	Stop Date	Avg. Time (h)	No. of Samples	Mean	Standard Deviation	Median	90th Per.	Max.
EC	Halifax	Bedford Row P.O.	09-Jun-89	08-Oct-90	24	65	3.7	1.3	3.7	5.7	6.8
EC	Halifax	1657 Barrington	07-Dec-90	10-Jun-98	24	399	3.5	1.8	3.1	5.6	13.8
EC	Kejimkujik Nat. Park		06-Jun-94	07-Sep-97	3,4,12	760	0.3	0.3	0.3	0.6	3.6
EC	Pt. Lepreau	Main Gate	05-Jul-92	16-Feb-98	24	285	0.4	0.2	0.4	0.7	1.2
EC	Saint John	Forest Hills	24-May-92	16-Feb-98	24	286	1.6	1.0	1.4	2.9	6.1
EC	Saint John	Forest Hills	08-Jul-92	27-Oct-92	3	154	2.5	2.2	2.0	4.9	11.8
EC	Ste. Francois		26-Feb-93	05-May-98	24	247	0.6	0.4	0.5	1.1	2.9
EC	Montreal	Pte. aux Trembles	16-Jan-89	03-Aug-98	24	495	9.0	9.3	6.1	20.0	126.3
EC	Montreal	Pte. aux Trembles	22-Jun-95	02-Sep-95	3	26	4.6	4.7	3.0	11.5	17.6
EC	Montreal	1125 Ontario St.	10-May-89	22-Jul-98	24	490	3.6	2.0	3.1	6.3	14.8
EC	Montreal	1001 Boul Maisonneuve O.	09-Jul-92	03-Aug-98	24	351	5.5	2.3	5.0	8.6	16.6
EC	Montreal	1001 Boul Maisonneuve O.	05-Jul-92	27-Oct-92	3	143	6.4	3.2	5.8	11.6	17.6
EC	Montreal	Parc Oceanie, Brossard	30-Jun-93	22-Jul-98	24	255	1.4	1.3	1.0	2.5	14.2
EC	Mount Sutton		06-Jun-94	26-Sep-98	3,4,12	867	0.4	0.3	0.3	0.7	3.2
EC	St. Anicet		15-Jun-94	30-Dec-97	3,4,12	728	0.5	0.5	0.4	1.0	4.4
EC	L'Assomption		27-May-96	30-Dec-97	3,4,12	321	0.9	0.8	0.7	2.1	4.9
EC	Ottawa	88 Slater St.	28-May-89	22-Jul-98	24	496	3.7	2.1	3.3	6.5	15.4
EC	Ottawa	Rideau/Wurtemburg	22-Sep-93	28-Jul-98	24	277	1.8	1.1	1.6	3.1	8.6
OME	Cornwall	Memorial Park	06-Apr-92	05-Dec-96	24	118	1.5	1.1	1.3	2.9	8.1
EC	Point Petre		25-Aug-96	16-Feb-98	24	87	0.6	0.3	0.6	0.9	2.0
OME	Dorset		19-Mar-91	17-Dec-96	24	151	0.4	0.3	0.4	0.8	1.3
OME	Oshawa	Ritson Road/Olive Ave	23-Jun-91	19-Feb-94	24	65	1.6	1.5	1.3	3.1	9.8
EC	Toronto	Bay/Grosvenor	06-May-92	18-Sep-95	24	203	2.7	1.3	2.4	3.9	10.4
EC	Toronto	Bay/Grosvenor	20-Jun-92	15-Sep-92	3	146	3.1	1.8	2.7	5.4	10.0
EC	Toronto	35 Edgar Ave.	04-Jan-89	25-Apr-93	24	192	2.8	2.1	2.2	5.0	18.8
EC	Toronto	Junction Triangle	04-Jan-89	04-Feb-98	24	444	2.5	1.6	2.2	4.0	16.6
OME	Toronto	Junction Triangle	16-Feb-90	02-Dec-92	3	59	1.3	1.3	0.9	2.5	6.8
EC	Toronto	Elmcrest Road	01-May-93	04-Feb-98	24	187	2.0	1.3	1.7	3.3	10.7
EC	Toronto	Elmcrest Road	05-Aug-95	18-Sep-95	3	12	2.1	1.3	1.7	4.0	4.3
EC	Toronto	Stouffville	10-Jan-89	04-Feb-98	24	414	1.4	4.0	0.9	2.1	77.1
EC	Toronto	Evans/Arnold	18-Jun-95	04-Feb-98	24	143	2.3	1.5	1.9	4.0	10.5
EC	Toronto	Evans/Arnold	15-May-95	02-Sep-95	3	60	1.8	1.2	1.5	3.4	6.4
OME	Toronto	Evans/Arnold	30-Jul-93	19-Feb-94	24	16	2.0	1.4	1.7	3.7	6.5
EC	Oakville	Bronte Rd./Woburn Cres.	27-Apr-95	02-Jun-96	24	22	1.7	1.2	1.6	3.4	5.3
OME	Oakville	Bronte Road/Woburn Cr	23-Jun-91	19-Feb-94	24	66	2.2	2.0	1.7	5.2	9.6
EC	Mississauga	Clarkson Refinery	02-Jul-96	04-Feb-98	24	80	1.6	0.8	1.5	2.5	5.3

Table 2 cont'd: Summary Statistics for Benzene (µg/m³): 1989 – 1998

Agency	City	Address	Start Date	Stop Date	Avg. Time (h)	No. of Samples	Mean	Standard Deviation	Median	90th Per.	Max.
OME	Mississauga	Meadow Park	23-Jun-91	19-Feb-94	24	69	3.3	2.8	2.6	6.1	19.0
EC	Egbert	CARE	14-Jun-94	17-Sep-98	3,4,12	881	0.5	0.4	0.4	1.0	3.8
EC	Hamilton	Elgin/Kelly	28-Jan-89	04-Jul-98	24	454	3.8	3.5	2.4	8.3	25.9
OME	Hamilton	Elgin/Kelly	16-Jan-90	17-Dec-96	24	179	3.5	4.4	2.1	6.7	44.8
OME	Hamilton	Beach Boulevard	05-Jul-91	05-Dec-96	24	132	4.7	3.7	4.2	9.3	23.2
OME	Hamilton	Gertrude/Depew	13-Mar-92	17-Dec-96	24	114	6.4	9.6	3.1	12.4	65.7
OME	Hamilton	Vicker's/East 18th	23-Jun-91	17-Dec-96	24	130	2.3	2.4	1.4	4.8	14.1
OME	Hamilton	Pier 25	25-Jan-92	17-Dec-96	24	125	4.3	3.4	3.4	8.5	16.2
EC	Nanticoke	Walpole School	25-Jan-93	09-May-94	24	64	1.4	1.0	1.1	2.1	6.4
OME	Nanticoke	Walpole School	14-May-94	17-Dec-96	24	65	1.0	0.7	0.8	1.7	4.0
EC	Nanticoke	Nanticoke Village	13-Jan-93	08-May-94	24	70	2.9	3.3	1.5	7.4	17.0
OME	Nanticoke	Nanticoke Village	14-May-94	17-Dec-96	24	71	2.1	2.4	1.0	5.6	12.8
EC	Simcoe	Experimental Farm	06-Feb-93	10-Jul-98	24	255	0.8	0.5	0.8	1.4	3.6
EC	Simcoe	Experimental Farm	18-Jun-94	30-Dec-97	3,4,12	674	0.7	0.4	0.6	1.2	3.3
OME	Elmira	Park/Duke	25-Apr-93	27-May-96	24	73	1.0	0.5	1.0	1.5	2.4
OME	London	King/Rectory	26-Jan-94	26-Jun-95	24	38	1.3	0.5	1.2	2.1	2.3
OME	London	Commissioner's Road	12-Apr-91	09-Dec-93	24	77	0.8	0.4	0.7	1.2	2.3
OME	London	Highbury Avenue	08-Jul-95	17-Dec-96	24	32	1.2	0.8	1.1	2.0	5.3
EC	Longwoods	Longwoods Cons. Auth.	12-May-91	10-Feb-98	24	332	0.8	0.4	0.7	1.3	2.8
EC	Sarnia	Centennial Park	10-Jan-89	10-Feb-98	24	464	3.6	4.6	1.9	9.0	37.4
EC	Windsor	467 University Ave.	04-Jan-89	08-Apr-94	24	295	2.9	1.6	2.4	4.8	11.7
EC	Windsor	467 University Ave.	03-Oct-92	27-Oct-92	3	40	3.8	2.3	3.4	6.6	10.4
OME	Windsor	467 University Ave.	04-Feb-90	17-Dec-96	24	168	1.8	1.3	1.5	3.5	8.5
EC	Windsor	College/Prince	29-May-90	29-Jan-98	24	438	2.3	1.5	1.9	4.1	13.0
EC	Windsor	College/Prince	20-Jun-92	02-Sep-95	3	190	1.9	2.0	1.3	3.5	19.9
OME	Windsor	Wright/Water	28-Jun-90	17-Dec-96	24	149	1.8	2.8	1.3	2.8	33.0
OME	Windsor	St. Gabriel's School	01-Jan-92	20-Mar-93	24	29	1.7	1.0	1.5	2.3	5.8
OME	Windsor	Geo. P. Vanier School	01-Jan-92	20-Mar-93	24	29	1.7	0.9	1.5	2.2	5.6
EC	Walpole Island		03-Feb-89	22-Mar-95	24	247	0.9	0.5	0.8	1.5	3.8
OME	S.S. Marie	Bonney St.	14-Jan-94	17-Dec-96	24	70	10.3	12.5	7.2	28.9	60.1
OME	S.S. Marie	Wm. Merrifield School	02-Oct-90	17-Dec-96	24	148	2.0	2.2	1.4	4.0	19.6
OME	Thunder Bay	James St. South	27-Oct-90	17-Dec-96	24	151	1.4	1.0	1.2	2.4	8.0
OME	Fort Frances	Church St.	08-Apr-94	17-Dec-96	24	66	0.9	0.4	0.8	1.4	2.5
EC	Winnipeg	65 Ellen St.	24-Dec-89	04-Jul-98	24	480	1.9	1.1	1.7	3.1	11.9
EC	Edmonton	17 St./105 Ave.	27-Aug-90	22-Jul-98	24	450	2.6	1.9	2.0	4.7	19.3
EC	Edmonton	10255-104th St.	18-May-91	22-Jul-98	24	420	3.1	1.8	2.6	5.4	13.5

Table 2 cont'd: Summary Statistics for Benzene (µg/m³): 1989 – 1998

Agency	City	Address	Start Date	Stop Date	Avg. Time (h)	No. of Samples	Mean	Standard Deviation	Median	90th Per.	Max.
EC	Calgary	611-4TH ST. SW	09-Aug-90	04-Jun-98	24	448	3.4	2.1	2.9	6.3	16.8
EC	Fort McMurray	MacDonald Drive	03-Apr-95	31-May-95	24	10	0.8	0.4	0.8	1.5	1.5
EC	Fort Saskatchewan	100 Ave. & 98th St.	28-Dec-94	02-Feb-95	24	4	2.9	3.6	1.6	8.2	8.2
EC	Vegreville	Royal Park	01-Aug-96	02-Nov-96	24	23	0.4	0.3	0.4	0.8	1.2
EC	Esther		25-Sep-96	30-Nov-96	24	16	0.3	0.2	0.3	0.6	0.7
EC	Vancouver	Robson Square	28-Jan-89	04-Feb-98	24	68	6.5	6.3	4.7	10.8	41.9
EC	Vancouver	Robson Square	06-Feb-93	19-Apr-93	3	56	6.1	2.6	5.8	9.4	13.3
EC	Vancouver	2550 W 10TH Ave.	26-Jul-93	06-Aug-93	24	6	3.5	1.3	3.5	5.9	5.9
EC	Vancouver	Kensington Park	04-Jan-89	17-Jan-98	24	80	4.2	2.8	3.4	9.1	12.4
EC	Vancouver	Kensington Park	09-Oct-92	27-Oct-92	3	32	7.0	3.5	6.3	12.1	13.5
EC	Vancouver	75 Riverside Dr.	22-Sep-93	09-Mar-94	3	92	3.8	2.5	3.0	7.2	13.1
EC	Vancouver	Rocky Point Park	04-Jan-89	04-Feb-98	24	510	4.2	3.0	3.5	8.2	21.5
EC	Vancouver	Rocky Point Park	05-Jul-92	02-Sep-95	3	170	3.3	2.3	2.6	6.5	12.3
EC	Vancouver	Surrey East	10-Jan-89	11-Jan-98	24	75	1.7	1.1	1.3	3.7	4.9
EC	Vancouver	Pitt Meadows Airport	15-Sep-92	03-Sep-95	3	196	1.1	0.9	0.7	2.3	4.3
EC	Vancouver	Richmond South	22-Jan-89	30-Dec-97	24	65	3.3	2.8	2.4	6.6	17.0
EC	Vancouver	Richmond South	01-Jan-93	28-Jul-93	3	31	5.9	4.9	4.7	11.3	23.4
EC	Vancouver	7815 Shellmount St.	18-Mar-90	17-Jan-98	24	184	2.6	1.8	2.0	5.1	11.4
EC	Vancouver	Mahon Park	23-May-90	23-Jan-98	24	61	2.4	1.7	1.9	4.3	9.5
EC	Vancouver	52nd. Ave. Langley	12-Jul-93	05-Jan-98	24	45	1.2	0.8	1.0	2.0	4.6
EC	Vancouver	52nd. Ave. Langley	31-May-93	02-Jun-95	3	245	1.1	0.9	0.8	2.5	5.6

Figure 2: Mean, 10th and 90th Percentile Benzene Concentrations by Site (1995-1997).

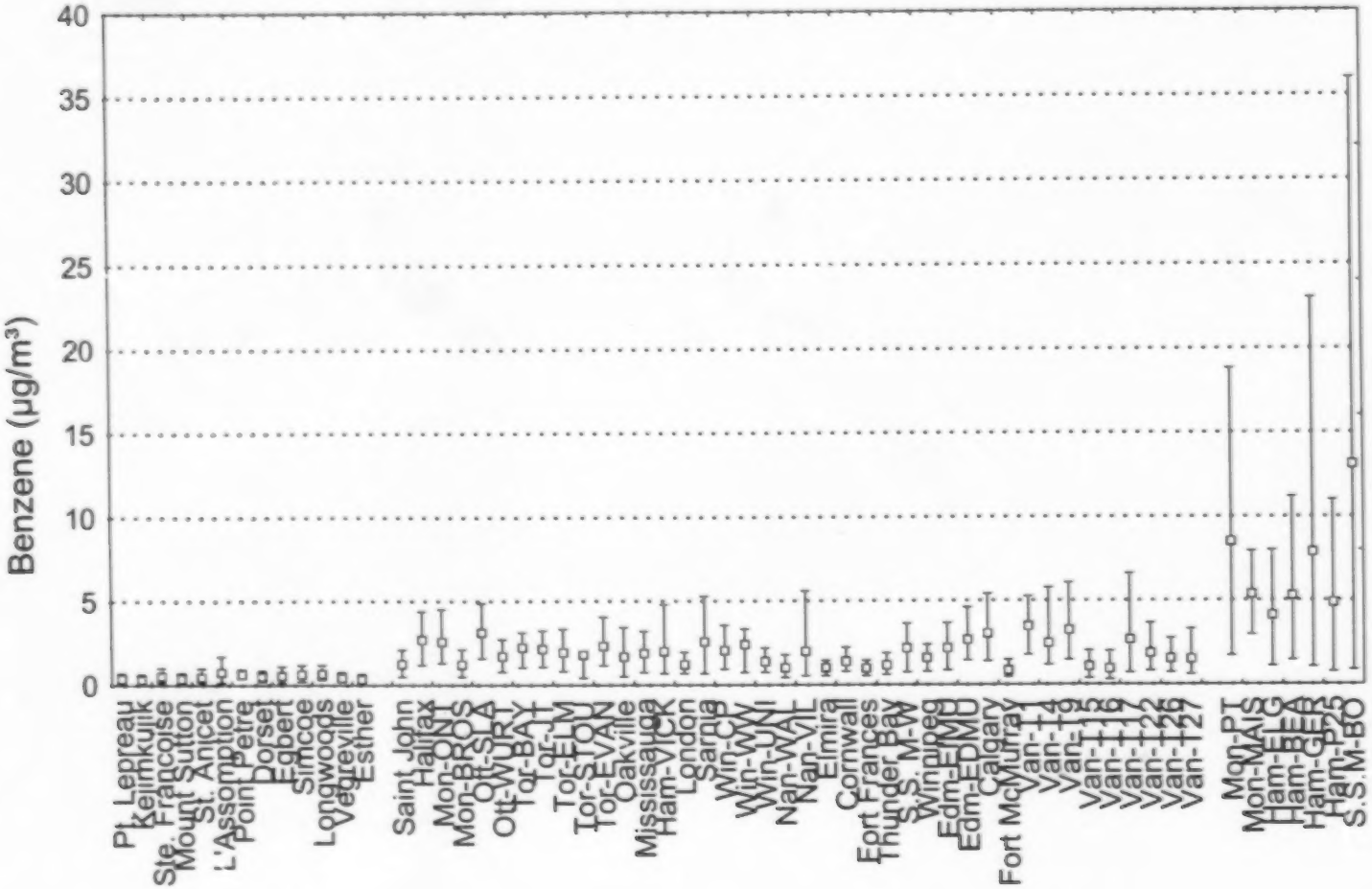
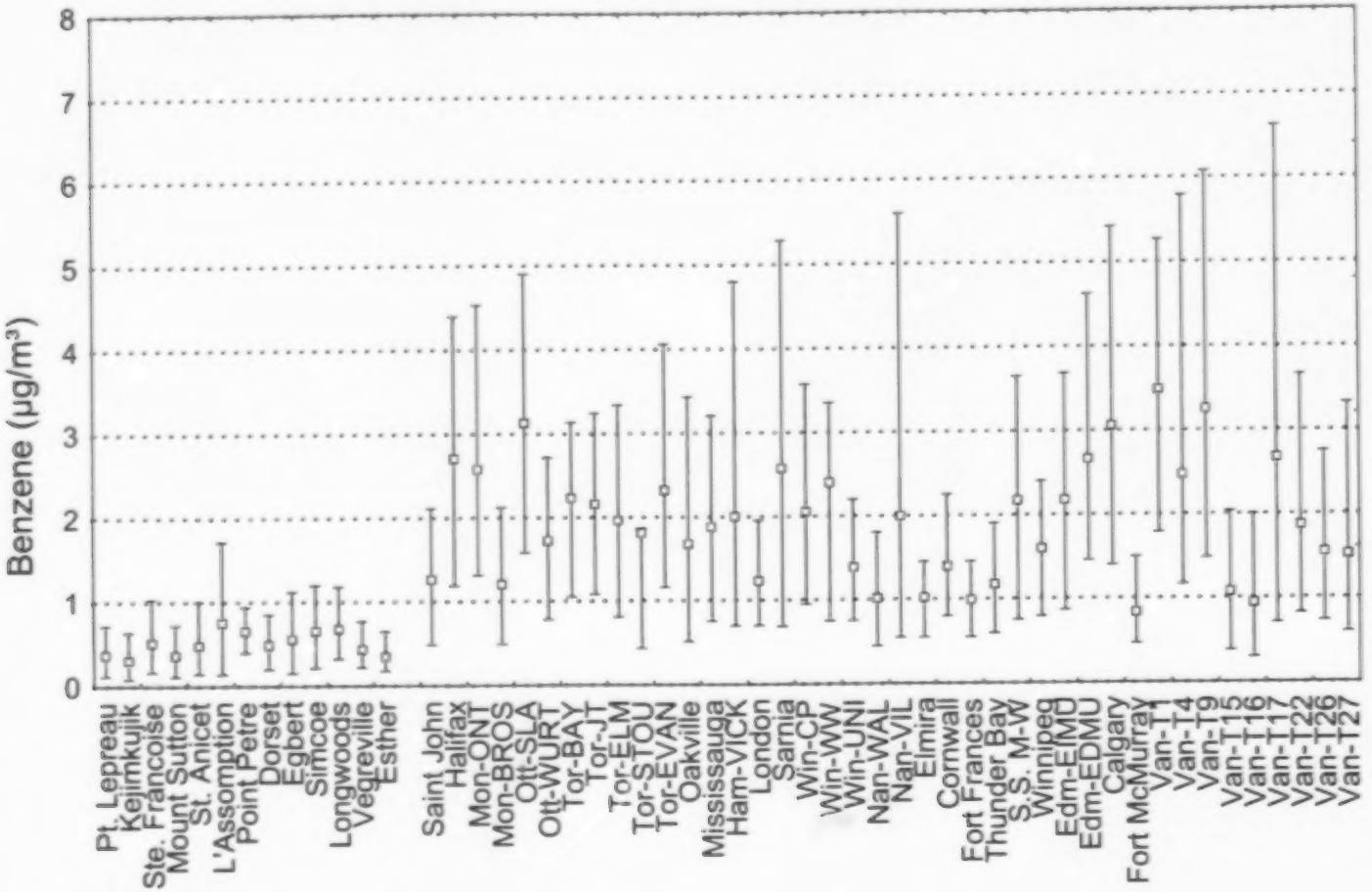


Figure 3: Mean, 10th and 90th Percentile Benzene Concentrations by Site (1995-1997) – Excluding Highest Sites.



Seasonal Variations

Seasonal differences in ambient benzene concentrations are determined by seasonal differences in emission rates, in meteorology (primarily wind speed, temperature and mixing depth) and in the rate of removal of benzene from the atmosphere. Benzene is considered of low reactivity in the atmosphere, and is removed only slowly by reaction with the OH radical. Residence times (defined as the time at which concentration is 37 % of original value) of benzene in urban atmospheres have been estimated to be 5 days in July and 120 days in January at 40°N latitude.[4] The difference is due to the much greater abundance of OH radicals in the summer. Residence times will be longer outside urban areas and at higher latitudes.

Monthly variations in benzene concentrations for eight rural sites with complete data for 1994/1997 (two data sets for Simcoe are shown – one is from 24 h 1-in-6-day sampling, the other from 12 and 4 hour sampling) are illustrated in Figure 4. All sites showed a typical seasonal pattern with minimum concentrations measured during June and July and maximum concentrations during January and February. Winter to summer ratios were approximately 3 at all sites. The Pt. Lepreau, Kejimkujik and Mount Sutton sites recorded the lowest benzene concentrations with the smallest variability. The Simcoe and Longwoods site showed the greatest variability in the summer months reflecting the impact of local sources. The January/February mean concentration of 0.8 $\mu g/m^3$ and June/July mean of 0.2 $\mu g/m^3$ at Pt. Lepreau are similar to a winter maximum benzene value of 0.8 $\mu g/m^3$ and a summer minimum of 0.1 $\mu g/m^3$ recorded in the free troposphere over the North Atlantic ocean.[5]

In Figure 5, monthly variations in benzene concentrations are shown for 12 urban sites (composite of 1990 to 1997 data). The Winnipeg, Calgary and Vancouver sites show the largest and most distinct seasonal variations in benzene concentrations. Most of the other urban sites recorded lower benzene concentrations in summer than in winter but variability is very large The point source influenced sites show site-specific seasonal patterns probably resulting from monthly variations in predominant wind directions.

Day of Week and Diurnal Variations

Day of week variations in benzene concentrations should be determined primarily by variations in day of week source emission strengths. In Figure 6 the day of week variation in benzene concentrations is given for the 12 urban sites. Urban sites typically experience lower median, 75th and 90th percentile benzene concentrations on Sundays and Saturdays. Benzene concentrations peak during mid week at most sites. Using results from these sites (Montreal-Trembles excluded) for 1990 to 1997, mean benzene concentrations for Thursday were 3.4 $\mu g/m^3$ versus 2.4 $\mu g/m^3$ for Sunday. Day of week changes in benzene concentrations were even larger for urban street sites such as Ottawa-Slater, with a factor of two difference in Thursday versus Sunday median benzene concentrations. Sites impacted by nearby industries, such as Sarnia, show a smaller difference between weekend and weekday benzene concentrations.

Only limited time of day measurements have been made at urban sites with most results coming from the summer of 1995. Diurnal plots are shown for selected urban sites in Figure 7. At most sites, benzene concentrations reach a minimum in the late afternoon due to better

atmospheric mixing. Many more diurnal observations have been made at rural sites. Data for the summer of 1995 are shown for selected rural sites in Figure 8. Most of the sites show highest concentrations overnight with minima experienced in mid to late afternoon.

Trends in Benzene Concentrations

Annual mean benzene concentrations are shown in Table 3 and 4 for two groupings of urban sites that met data completeness criteria for the period 1990 to 1997 (at least 20 observations in each year and 7 out of 8 years of data) or for 1992 to 1997 (at least 20 observations in each year and 5 out of 6 years of data).

Using the composite results for 1990 to 1997 there was a 25% reduction in annual mean benzene concentrations between 1990 and 1995 followed by a small increase between 1996 and 1997. The composite data are also shown in the form of a boxplot analysis in Figure 9. This figure also shows steadily declining median and 75th percentile values between 1990 and 1995, followed by no change in median concentrations between 1995 and 1997 but an increase in 75th and 90th percentile concentrations. Results for individual sites are quite variable as shown in Table 5 with percentage reductions between 1990 and 1996 ranging from 0 to 50 %. The site with the highest mean concentration (Montreal-Trembles) showed no improvement over the period.

For the 1992 to 1997 data sets, composite annual means decreased by 24% for the EC sites and increased by 21% for the OME sites between 1992 and 1996. The OME results are dominated by results for Hamilton however. Figure 10 shows the EC composite results in the form of a boxplot. A similar result was obtained for this grouping of sites with declines between 1992 and 1995 followed by no significant change from 1995 to 1997 in median concentrations and a small increase in 75th and 90th percentile concentrations. All but 4 of the EC sites showed declines in benzene between 1992 and 1996 with percentage decreases ranging from 7 to 55%. Two sites showed no change and two sites (Montreal-Trembles and Windsor-College) recorded increases in mean benzene concentrations between 1992 and 1996. Ten out of eighteen sites had an increase in mean benzene concentration between 1996 and 1997. For the OME sites, four out of five Hamilton sites showed increasing mean benzene concentrations.

The Ottawa-Slater and Vancouver-Rocky Point site recorded some of the largest decreases in benzene levels over the period. Figures 11 and 12 compare benzene levels during 1990-1992 and 1995-1997 by day of week for these two sites. Both sites show that the largest changes in benzene concentrations occurred during mid week with the smallest change on Sunday.

In Table 5, annual mean benzene concentrations for rural sites with complete data (24-h samples for at least 20 days of observations in each year and 3 out of 4 years of data) for 1994 to 1997 are shown. Most of the rural sites showed little change in mean benzene concentrations over the period. Three of four sites showed a small increase from 1996 to 1997.

A complete emission inventory trend analysis has not yet been completed, but the decline in ambient benzene levels at most urban sites is a result of improved VOC emission control technology on new motor vehicles plus the effect of reduced gasoline benzene levels. The relationship between emissions and ambient levels of benzene will be explored in a later report.

Figure 4: Monthly Variation in Benzene at Rural Sites (1994-1997).

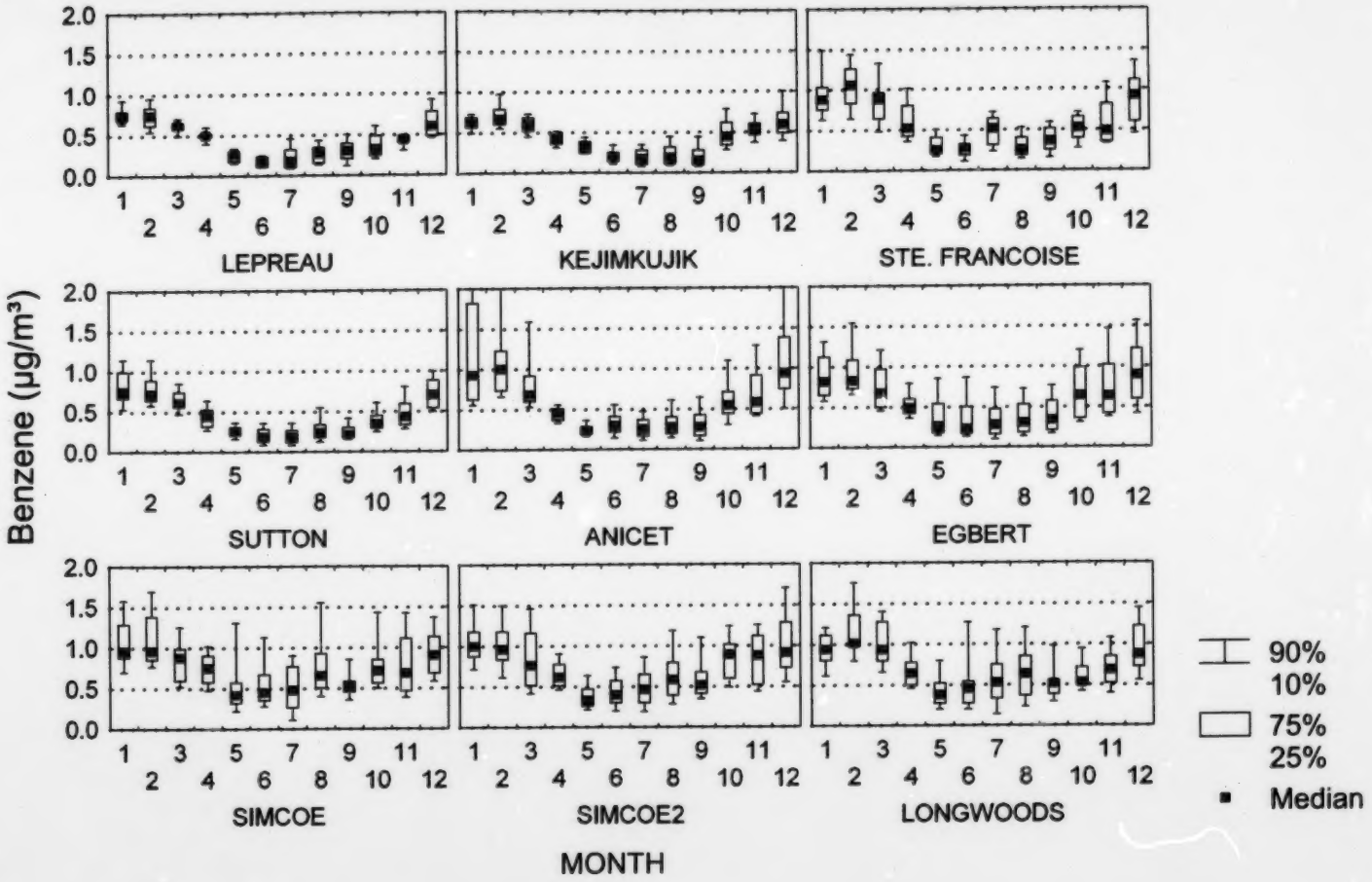


Figure 5: Monthly Variation in Benzene at Suburban and Urban Sites (1992-1997).

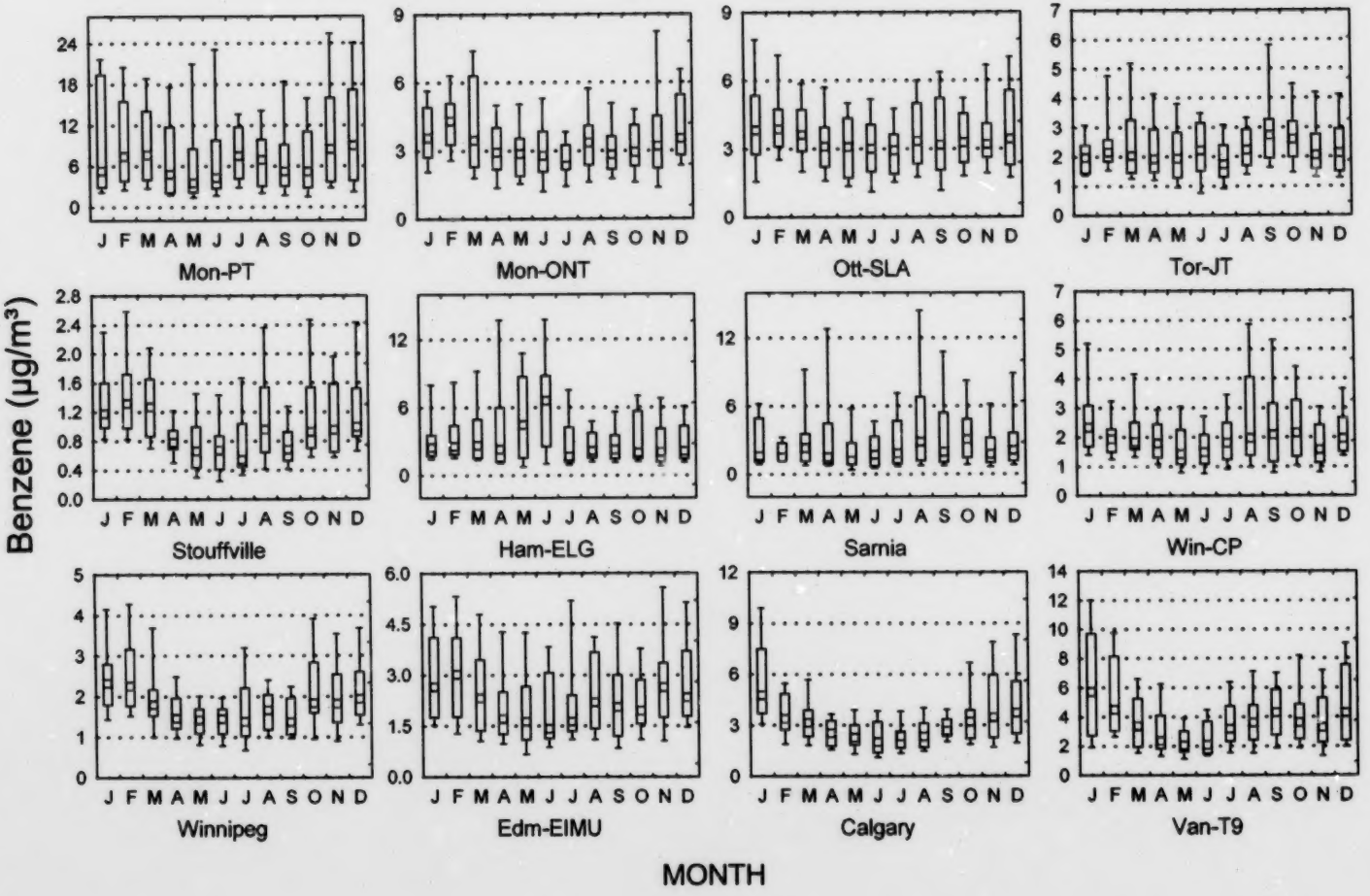


Figure 6: Day of the week Variation in Benzene at Urban Sites (1990-1997).

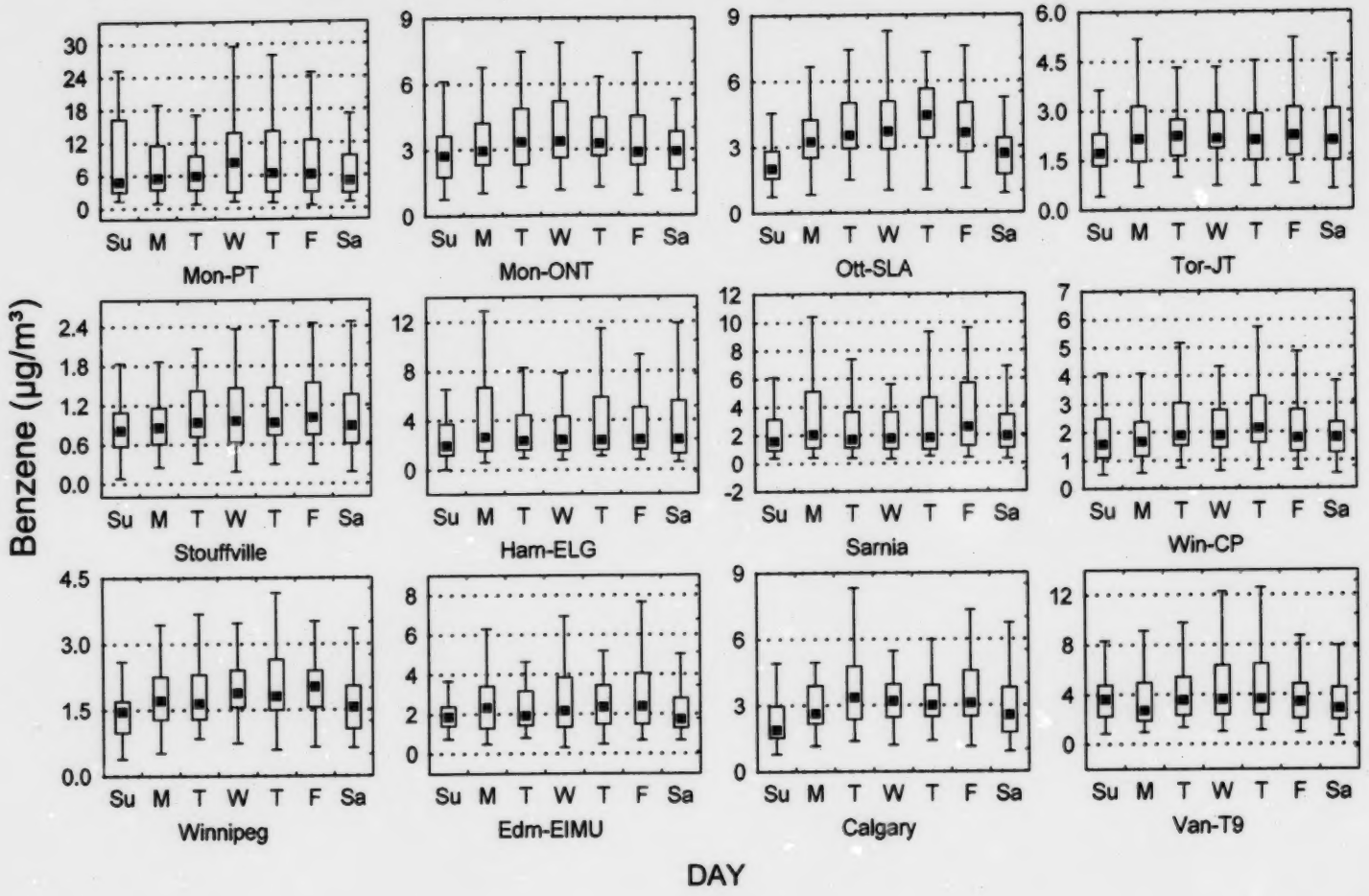


Figure 7: Diurnal Variations in Benzene Concentrations at Urban Sites (1995).

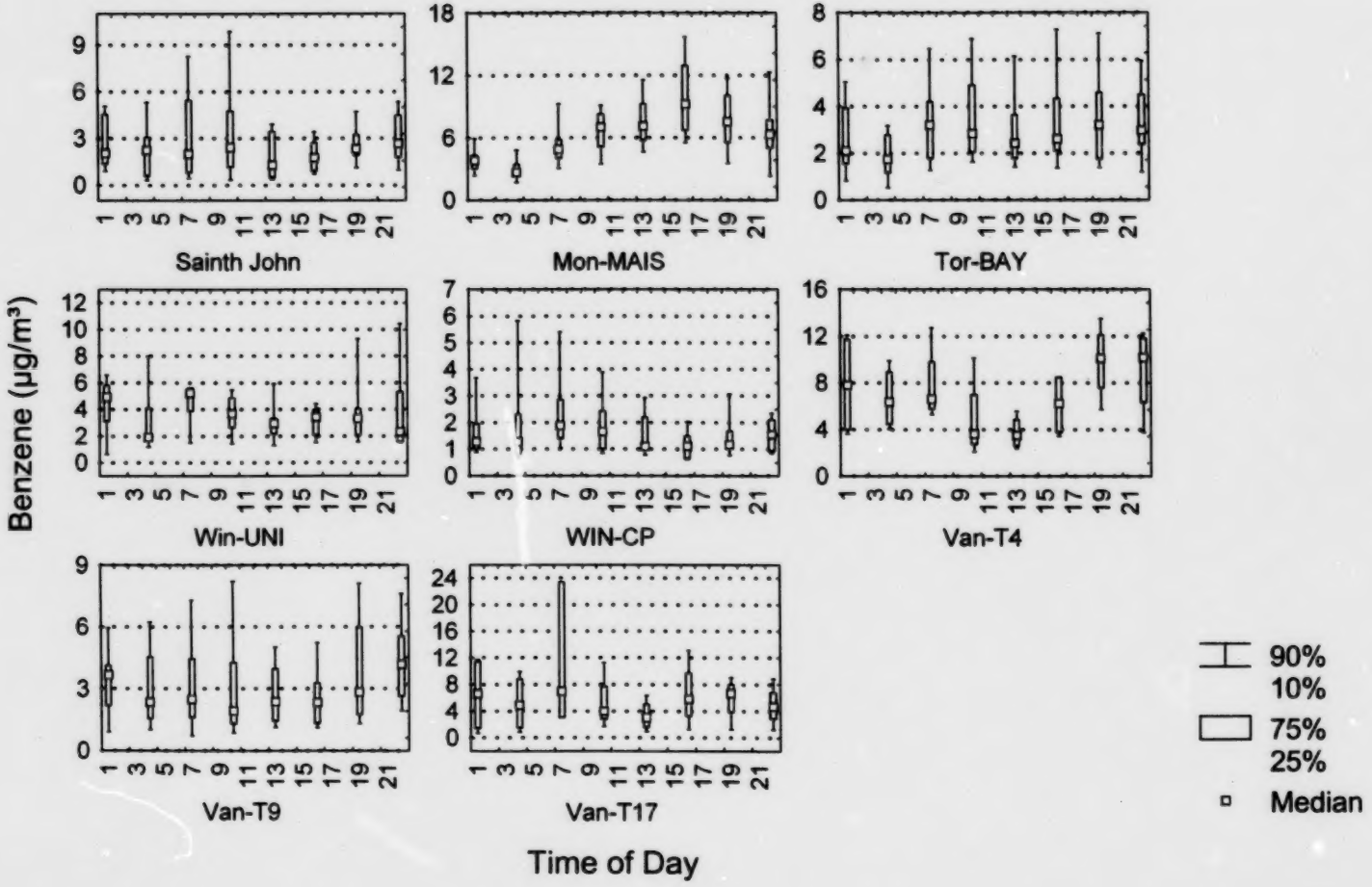


Figure 8: Diurnal Variations in Benzene Levels at Rural Sites (Summer of 1995).

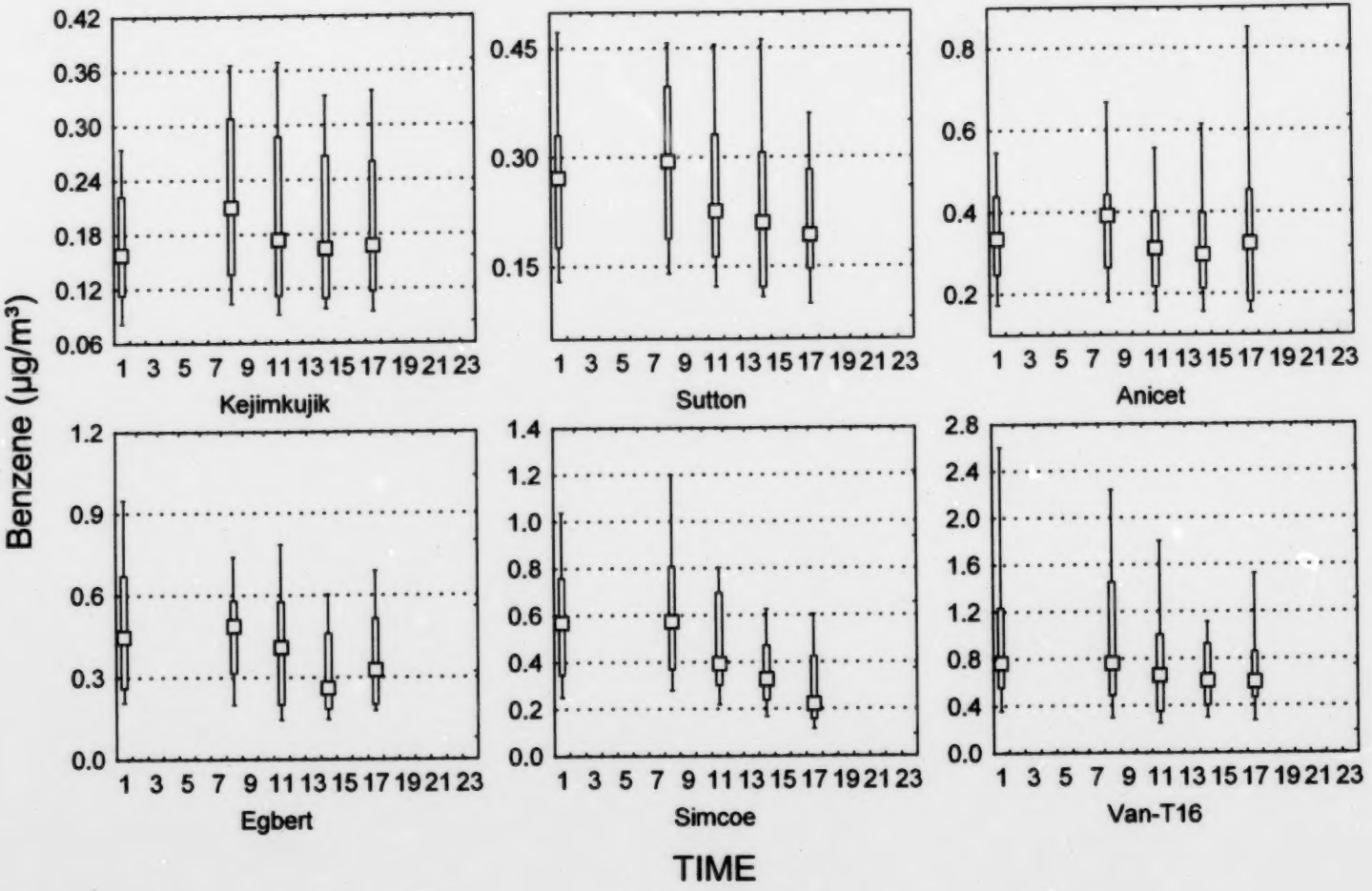


Table 3: Annual Mean Benzene Concentrations for 1990 to 1997 for Urban and Suburban Sites (EC Only)

Station	City	1990	1991	1992	1993	1994	1995	1996	1997
50103	Montreal	8.0	9.7	7.4	10.0	8.5	9.0	8.1	11.4
50104	Montreal	4.3	4.3	4.2	4.0	3.6	2.4	2.7	3.0
60101	Ottawa	4.6	3.8	4.1	4.0	3.9	2.9	3.3	3.2
60211	Windsor	2.7	2.4	2.0	2.4	2.2	1.9	2.2	2.8
60418	Toronto	2.7	2.5	2.5	2.2	3.1	2.0	2.3	2.3
60512	Hamilton	4.8	3.5	4.6	4.3	3.7	2.4	3.9	2.9
61004	Sarnia	5.3	4.7	3.6	2.6	4.2	2.0	3.2	2.4
63201	Toronto	1.3	1.2	1.1	1.0	1.3	2.6	1.1	1.4
70119	Winnipeg	2.5	2.0	2.4	2.1	1.8	1.7	1.5	1.5
90121	Edmonton	3.1	3.1	3.4	2.9	2.6	2.6	1.8	2.1
90227	Calgary	3.1	4.5	3.9	3.4	3.2	3.4	2.7	2.9
100111	Vancouver	5.6	4.7	4.4	4.7	3.6	3.7	2.8	2.8
Average		4.0	3.9	3.6	3.6	3.5	3.0	3.0	3.2

Figure 9: Yearly Variations in Benzene for Urban Sites (1990-1997).

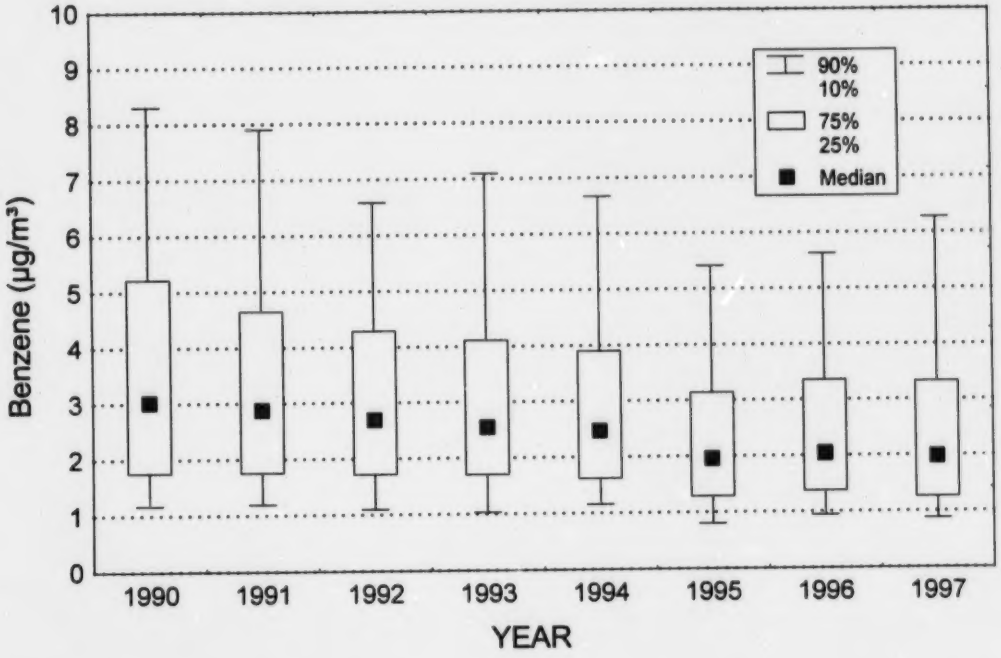


Table 4: Annual Mean Benzene Concentrations for 1992 to 1997 for Urban and Suburban Sites (EC and OME)

Agency	NAPS ID	City	1992	1993	1994	1995	1996	1997
EC	30118	Halifax	4.5	4.1	3.3	2.5	2.9	3.0
EC	40203	Saint John	1.9	1.7	1.6	1.3	1.3	1.9
EC	50103	Montreal	7.4	10.0	8.5	9.0	8.1	11.4
EC	50104	Montreal	4.2	4.0	3.6	2.4	2.7	3.0
EC	50115	Montreal	5.6	6.1	5.4	5.1	5.6	5.5
EC	50121	Montreal	-	1.8	1.7	1.1	1.3	1.3
EC	60101	Ottawa	4.1	4.0	3.9	2.9	3.3	3.2
EC	60211	Windsor	2.0	2.4	2.2	1.9	2.2	2.8
EC	60418	Toronto	2.5	2.2	3.1	2.0	2.3	2.3
EC	60512	Hamilton	4.6	4.3	3.7	2.4	3.9	2.9
EC	61004	Sarnia	3.6	2.6	4.2	2.0	3.2	2.4
EC	63201	Toronto	1.1	1.0	1.3	2.6	1.1	1.4
EC	70119	Winnipeg	2.4	2.1	1.8	1.7	1.5	1.5
EC	90121	Edmonton	3.4	2.9	2.6	2.6	1.8	2.1
EC	90130	Edmonton	4.0	3.6	3.5	2.7	2.6	2.3
EC	90227	Calgary	3.9	3.4	3.2	3.4	2.7	2.9
EC	100111	Vancouver	4.4	4.7	3.6	3.7	2.8	2.8
EC	100133	Vancouver	3.9	3.4	2.6	1.9	1.8	1.9
EC	Average		3.7	3.6	3.3	2.8	2.8	3.0
OME	60204	Windsor	1.9	1.2	1.2	1.4	-	-
OME	60212	Windsor	1.9	1.3	1.3	1.4	1.4	-
OME	60511	Hamilton	4.0	3.4	4.3	5.8	4.6	-
OME	60512	Hamilton	4.2	2.8	2.3	3.0	5.5	-
OME	60513	Hamilton	3.8	1.9	1.9	1.9	2.1	-
OME	-	Hamilton	3.7	4.1	4.0	5.1	4.5	-
OME	-	Hamilton		3.8	6.3	8.1	7.6	-
OME	60707	S.S. Marie	1.5	2.0	2.0	1.6	2.8	-
OME	60807	Thunder Bay	1.6	1.2	1.1	1.3	1.0	-
OME	61201	Cornwall		1.8	1.4	1.4	1.4	-
OME	Average		2.8	2.4	2.6	3.1	3.4	-

Figure 10: Yearly Variations in Benzene for EC Urban Sites (1992-1997).

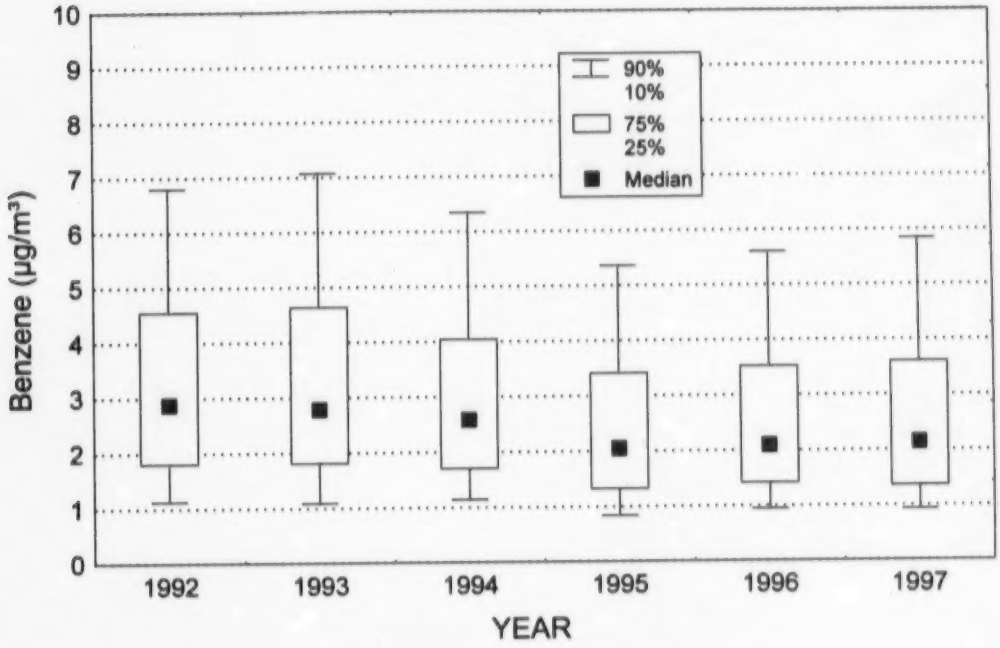


Figure 11: Day of week Variation in Benzene for Ottawa Slater street Site (1990-92 vs. 1995-1997).

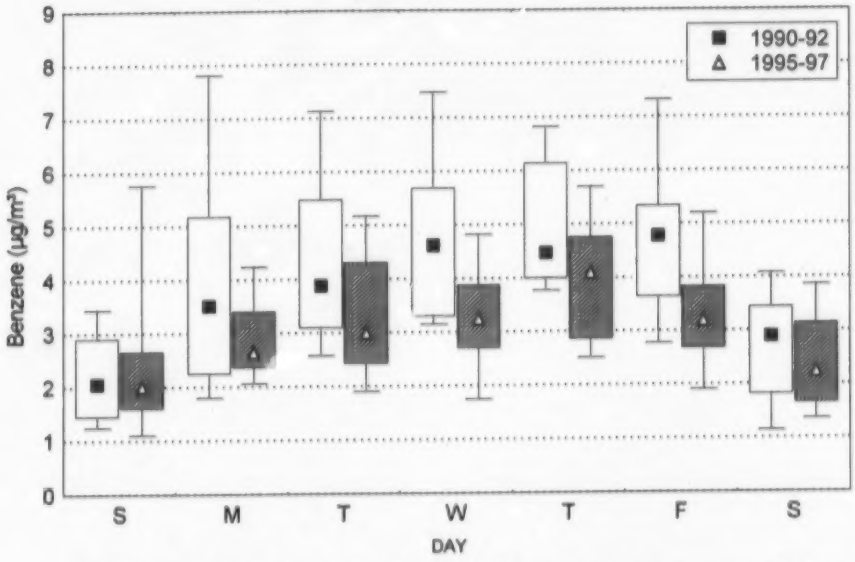


Figure 12: Day of week Variation in Benzene for Vancouver Rocky Point Park Site (1990-92 vs. 1995-1997).

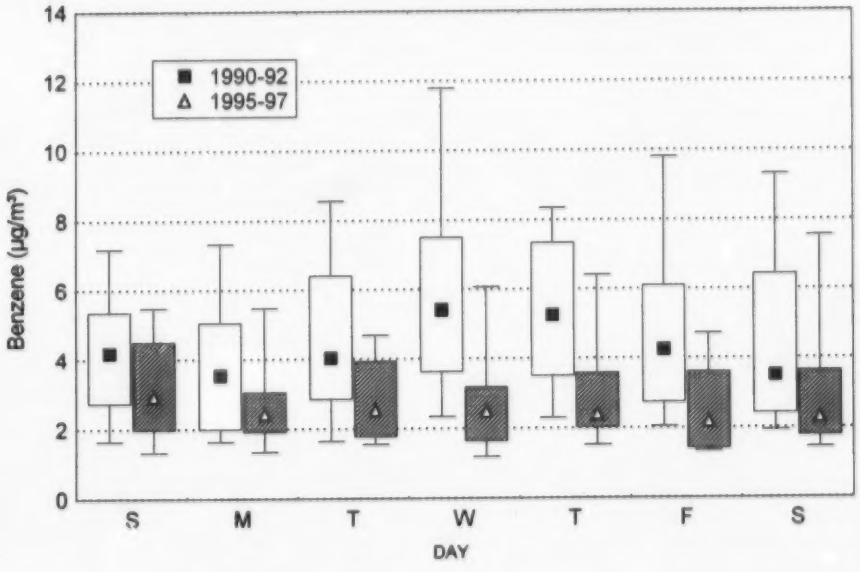


Table 5: Annual Mean Benzene Concentrations for 1994 to 1997 for Rural Sites

NAPS ID	Location	1994	1995	1996	1997
54301	Ste. Francoise	0.77	0.49	0.54	0.64
40501	Pt. Lepreau	0.47	0.35	0.39	0.53
62601	Simcoe	0.69	0.60	0.66	0.71
63601	Longwoods	1.00	0.63	0.75	0.68
63301	Dorset	0.35	0.48	0.50	-
Average		0.66	0.51	0.57	0.64

Conclusions

An extensive database of ambient air benzene observations is available for Canada for the 1989 to 1998 time period. Mean benzene concentrations (using data for all years) ranged from 10.3 $\mu g/m^3$ at an urban site influenced by emissions from a coke oven/iron and steel mill facility (Sault Ste. Marie-Bonney St.) to 0.3 $\mu g/m^3$ at a rural remote site (Kejimkujik National Park in Nova Scotia). For typical (i.e. not adjacent to roadways) urban site locations with no industrial source influences, mean benzene concentrations over the period were in the range of 1.8 to 3.6 $\mu g/m^3$. Mean and median benzene concentrations are highest at urban-street sites and at sites influenced by industrial sources and lowest at rural and suburban sites.

For the most recent years of measurements (1995 to 1997), mean concentrations at the urban/suburban sites ranged from 1.0 to 3.5 $\mu g/m^3$ with most sites (31 out of 40) recording mean concentrations of less than 2.5 $\mu g/m^3$. Ninetieth percentile concentrations at these sites ranged from 1.5 to 6.6 $\mu g/m^3$ with most sites (31 out of 40) recording 90th percentile concentrations of less than 4.5 $\mu g/m^3$. For the rural sites mean concentrations ranged between 0.3 and 0.8 $\mu g/m^3$ with 90th percentile concentrations ranging between 0.6 and 1.7 $\mu g/m^3$. For sites near roadways or near industrial sources, mean benzene concentrations ranged from 4.1 to 13.1 $\mu g/m^3$ and 90th percentile concentrations varied from 8.0 to 36.0 $\mu g/m^3$.

Most sites recorded decreases in benzene concentrations between 1990 and 1997. Using the composite results for urban sites with complete data there was a 25% reduction in annual mean benzene concentrations between 1990 and 1995 followed by a small increase between 1996 and 1997. Results for individual sites are quite variable with percentage reductions between 1990 and 1996 ranging from 0 to 50 %. A number of sites with the highest mean concentrations showed little or no improvement over the period.

A complete emission inventory trend analysis has not yet been completed, but the decline in ambient benzene levels at most urban sites is a result of improved VOC emission control technology on new motor vehicles plus the effect of reduced gasoline benzene levels. The relationship between emissions and ambient levels of benzene will be explored in a later report. The lack of improvement in benzene levels at some sites with high concentrations will also be investigated.